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The United States ocean dumping regulations developed pursuant to PL 92-532, the Marine Protection, Research, and Sanctuaries Act of 1972, as amended, provide for a general policy of isolation and containment of low-level radioactive waste after disposal into the ocean.

In order to determine whether any particular waste packaging system will meet this general requirement, and for how long, it is necessary to know what materials were used and how those materials will behave in the deep sea.

This report discusses the mechanisms of marine corrosion of structural and stainless steels, the degradation mechanisms acting on concrete in a marine environment, the interaction between metal and concrete combined as a low-level radioactive waste package under deep sea conditions, and the effect of environmental parameters such as dissolved oxygen, temperature, and water velocity on deep sea degradation processes. A concluding discussion presents various improved metal alloys and concrete additives which may result in greater resistance of a low-level radioactive waste package to deep sea deterioration processes.

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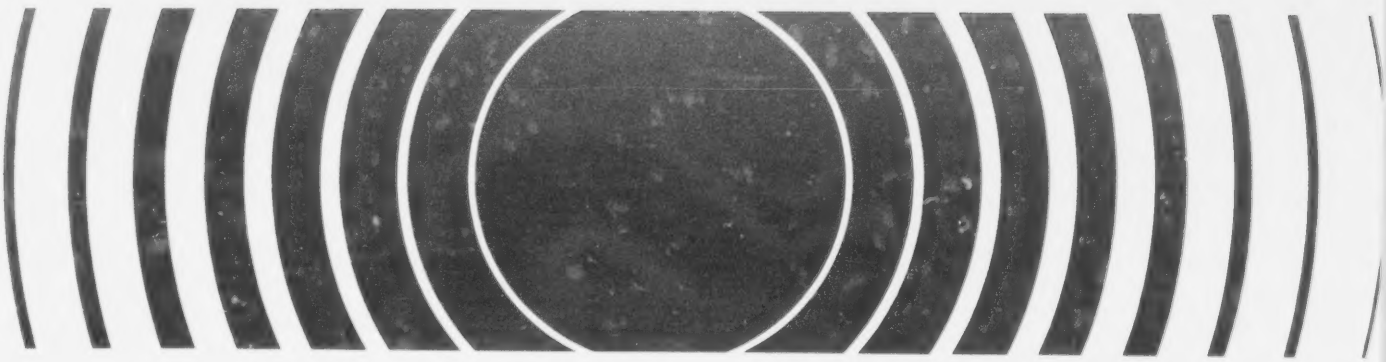

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MATERIALS FOR CONTAINMENT OF LOW-LEVEL NUCLEAR WASTE IN THE DEEP OCEAN

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Project Officer

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Analysis and Support Division
Office of Radiation Programs
U.S. Environmental Protection Agency
Washington, D.C. 20460

FOREWORD

In response to the mandate of Public Law 92-532, the Marine Protection, Research and Sanctuaries Act of 1972, as amended, the Environmental Protection Agency (EPA) has developed a program to promulgate regulations and criteria to control the ocean disposal of radioactive wastes. As part of that program, the EPA Office of Radiation Programs initiated feasibility studies in 1974 to learn whether present technologies could be used to determine the fate of radioactive wastes dumped in the past.

After successfully locating radioactive waste drums in previously used United States dumpsites, the Office of Radiation Programs developed a program of dumpsite-specific studies to look at the biological, chemical, and physical characteristics of the sites, and the presence and distribution of radionuclides within these sites. The Office also has an ongoing effort to evaluate the low-level radioactive waste packaging techniques and materials used in the past, with a view towards developing packaging performance criteria and recommendations for improved packaging materials and design.

As part of this development process, the Office has initiated a generic study to describe the various corrosion and degradation processes that would be expected to affect a waste package in the deepsea. This report presents some preliminary results of that ongoing study. Based upon these preliminary results, an estimate can be made of the expected lifetime of a conventional metal drum containing a concrete matrix. This information can then be compared with the empirical results of the separate, detailed analyses of various low-level radioactive waste packages recovered from the ocean under the direction of this Office, and any differences will be examined.

Readers of this report are encouraged to inform Mr. David E. Janes, Director, Analysis and Support Division (ANR-461), Office of Radiation Programs, U.S. Environmental Protection Agency, Washington, D.C. 20460, of any errors, omissions, or other comments pertinent to improving this document.

Glen L. Sjoblom

Glen L. Sjoblom, Director
Office of Radiation Programs

ABSTRACT

During the period between 1946 and 1970 the United States carried out sea disposal of low-level radioactive waste. A low-level waste package was developed consisting of a plain carbon structural steel 55-gallon cylindrical drum into which the radioactive material and a concrete matrix was admixed. The present report examines the electrochemical processes which corrode metals in saltwater, factors affecting corrosion rates in the deep sea, and mechanisms which degrade concrete immersed in seawater. Environmental data is reviewed on the rates and interactive nature of these corrosion and degradation mechanisms. For the purposes of this report, failure of the container is considered to have occurred as soon as seawater is allowed to contact the waste. Based on this criterion, it is concluded that the lifetime of conventional containers is likely to be short compared to the ten half-life (50-300 years) minimum isolation period that has been considered for key radioactive components of low-level waste, such as strontium-90, and cesium-137. The concept for an improved cost-efficient container capable of isolating wastes for 50 to 75 years with a high degree of reliability is presented. However, it is emphasized that our present knowledge of the mechanisms and rates of deterioration of structural materials in the deep ocean is insufficient to guarantee the integrity of even the improved containers for upwards of 300 years.

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1.0 INTRODUCTION

The two classes of materials that have historically been used for packaging low-level nuclear waste for ocean disposal are plain carbon structural steel and concrete. These were usually arranged in the form of a two- or three-layered container starting on the outside with a 55- or 80-gallon structural steel oil drum from which one end had been removed. First, the drum was partially filled with concrete. The waste form itself was pressed into the wet concrete and the drum then filled with more concrete. Some types of low-level liquid waste were mixed directly with the concrete in the steel drum.[1] Occasionally the waste form itself was a contaminated or activated piece of plain carbon or stainless steel, which was pressed into the wet concrete. In this latter case, the steel or stainless steel waste form would act as an additional containment barrier in that radionuclides would be released to the environment only through corrosion of the steel or stainless steel itself. Thus, a third class of materials which must be considered, in addition to the concrete and steel mentioned above, are the stainless steels.

It is assumed throughout this report that typical low-level nuclear wastes must be isolated from man and his food chain for a minimum period of time corresponding to ten half-lives of the waste. For example, for low-level wastes containing Cs-137 or Sr-90 this containment period would be a minimum of 300 years, and 280 years respectively. Other wastes having shorter half-lives (e.g. Co-60) would need to be isolated for upwards of 50 years. It is further assumed that public opinion will not long tolerate any waste disposal program in which there is even a small percentage of containment failures that result in premature

release of the waste to the marine environment before the end of the appropriate minimum containment period.

All three classes of materials mentioned above are known to be susceptible to deterioration in seawater environments. The degradation mechanisms begin immediately upon immersion of these materials in seawater, and appreciable deterioration by corrosion can occur in as little as one or two years for steel and stainless steel, and in 5 to 20 years for concrete. These times are much shorter than the 50 to 300 year minimum containment period for the radionuclides discussed above. The purposes of this report are, therefore, to (1) summarize the current literature on the seawater degradation of these materials, (2) assess what the lifetime of these materials is likely to be in the deep sea and in the configurations used for packaging nuclear wastes, and (3) suggest possible alternative packaging techniques and materials.

From an engineering point of view, the purpose of the outer steel container is primarily to serve as a convenient mold for the concrete. Before it starts to corrode appreciably, the steel container also provides a partial barrier between the concrete and seawater. In past ocean dumping this was a minor function for steel because the packages left the concrete exposed directly to seawater at the open end of the drum. Therefore, functionally, it matters little whether or not the steel corrodes. Deterioration of the concrete and the metals of the waste form itself are a more serious matter, as they are the materials which are called upon to isolate the waste.

In the following sections, the appropriate deterioration mechanisms will be outlined, the available environmental data on degradation rates will be summarized, the expected lifetime of the conventional types of

containers will be estimated from these data, and several alternatives to the present methods of containment will be discussed.

2.0 DETERIORATION MECHANISMS

2.1 CORROSION OF METALS

Basic Mechanism

Degradation of metallic materials in marine environments by corrosion can take several forms, but all of them are electrochemical in nature. That is, the process involves the simultaneous transfer of electrical charges in the metal, and ions in the electrolyte (seawater in this case) into which the metal is placed.

The corrosion process takes place at two distinctly different types of sites on the metal surface. At the first of these sites, called the anode, chemical oxidation takes place, and metal ions leave the surface of the metal to enter the solution as illustrated in Figure 1. It is this loss of metal ions at the anode that leads to structural damage of the metal during corrosion. Of equal importance is the second site, called the cathode, where chemical reduction takes place and dissolved oxygen from the seawater is reduced to hydroxyl ions (OH^-). As iron atoms are oxidized to Fe^{++} at the anode they liberate electrons which travel through the metal and are consumed in the reduction at the cathode (Figure 1). A simple chemical equation describes each of these reactions as follows:

At the anode: $2Fe - 4e^- \rightarrow 2Fe^{++}$

At the cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Combining the two, we can write the overall reaction as:

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe^{++} + 4OH^- \rightarrow 2Fe(OH)_2$$

The product of this reaction, $Fe(OH_2)$, is a hydrated ferrous oxide or

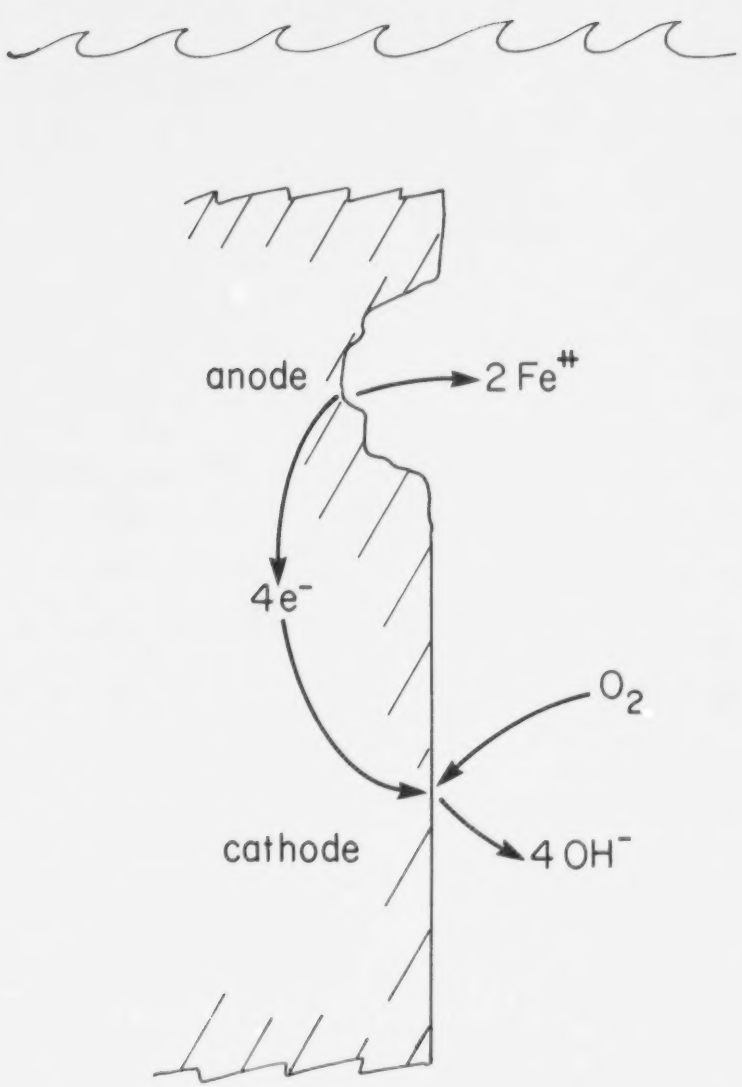

FIGURE 1. Electrochemical reactions at anodic and cathodic sites on structural steel corroding in seawater.

ferrous hydroxide. It is insoluble and forms a loosely adherent green or greenish black surface film on steel in seawater. The outer surface of the film, which is in contact with a ready supply of dissolved oxygen, is further oxidized to ferric hydroxide by the reaction:

$$2Fe(OH)_2 + H_2O + 1/2\ O_2 \rightarrow 2Fe(OH)_3$$

This is orange to reddish brown in color and is familiar to us as common rust.

Structural Steel

On plain carbon structural steel, the anode and cathode areas described above shift about continuously on the metal surface. The result is called "uniform corrosion". The surface becomes generally rusted and the metal thickness is reduced almost uniformly over the entire exposed surface. It is this type of corrosion to which the outer steel drum of past nuclear waste packaging containers is subjected. Uniform corrosion of structural steel in seawater will be accelerated if the steel is brought into direct contact with a more noble (cathodic) metal such as a copper alloy, stainless steel, or titanium. This type of attack, called galvanic corrosion, or electrolysis, will be described in the following paragraphs.

When two different metals are placed in direct contact in seawater, a difference in electrochemical potential exists between them. This potential difference causes a corrosion current to flow. The more active of the two metals becomes the anode and begins to corrode more rapidly than it would by itself. The more noble metal becomes the cathode and is protected from corrosion. The accelerated corrosion on the less noble (anodic) metal is called galvanic corrosion. Table I shows a "galvanic series" of common metals and alloys in seawater.[2]

TABLE I

GALVANIC SERIES OF METALS AND ALLOYS
IN SEAWATER

Alloy	Potential vs. Satd. Calomel Electrode
ANODIC END	
Magnesium	-1.60 to -1.63V
Zinc	-0.98 to -1.03V
Aluminum Alloys	-0.70 to -0.90V
Cast Iron	-0.60 to -0.72V
Steels (structural and alloy)	-0.57 to -0.70V
Stainless Steels (active-i.e. in crevices & pits)	-0.35 to -0.57V
Al - Bronze D	-0.30 to -0.42V
Naval Brass	-0.30 to -0.40V
Red Brass	-0.20 to -0.40V
Copper (ETP)	-0.28 to -0.36V
Inhibited Admiralty Brass	-0.25 to -0.34V
Manganese Bronze A	-0.25 to -0.33V
Silicon Bronze	-0.24 to -0.27V
90-10 Copper Nickel	-0.21 to -0.28V
Type 400 Stainless Steels (passive)	-0.20 to -0.28V
Lead	-0.19 to -0.25V
70-30 Copper Nickel	-0.13 to -0.22V
17/4 pH Stainless Steel (passive)	-0.10 to -0.20V
Silver	-0.09 to -0.14V
Monel 400 (Nickel-copper alloy)	-0.04 to -0.14V
Type 300 Stainless Steels (passive)	-0.00 to -0.15V
Stainless Alloy 20 cb3	+0.05 to -0.15V
Titanium and Titanium Alloys	+0.06 to -0.05V
Inconel 625	+0.10 to -0.04V
Hastelloy C-276	+0.10 to -0.04V
Stainless Alloy 6X (passive)	+0.32 to -0.15V
Tantalum	about +0.2V
Platinum	+0.35 to +0.2V
Graphite	+0.3 to +0.2V
CATHODIC END	

For any combination of metals, the galvanic series can be used to predict which metal will suffer accelerated attack (anode) and which metal will be protected (cathode). If any two metals or alloys from Table I are placed in contact in seawater, the one higher on the series will be the anode, and the severity of the damage to it will be directly proportional to the magnitude of the potential difference between the two metals, or simply the separation of the two metals or alloys on the chart. Two examples illustrate this point. If steel is coupled to Monel 400 (nickel-copper alloy), the steel will be anodic and will be damaged severely because the two alloys are far apart on the chart. If copper and silicon bronze are coupled, damage will be slight because they are close together on the chart; that is, the two metals have a small potential difference.

It is possible to take advantage of galvanic corrosion by coupling a material one wishes to protect from corrosion to a more active metal. For instance, steel can be protected from corrosion in seawater by coupling it to zinc. The zinc in this case is called a sacrificial anode, and the steel will be protected as long as any zinc remains. The protection can be extended indefinitely by periodically replacing the zinc anodes if the structure is accessible for maintenance.

Stainless Steels

The behavior of stainless steels is quite different from that described above. Stainless steels contain 12% or more of chromium, which make them "passive," or resistant to uniform corrosion. Their passivity in seawater is caused by the formation of a tightly adherent surface film of metal oxide. Other alloying elements in addition to chromium are often added to make this passivity more stable in a wide range

of environments or to enhance the mechanical and physical properties, or both. Nickel and molybdenum are two alloying elements commonly added to stainless steels intended for seawater service. The class of stainless steels most frequently used around marine environments in the past, the 300-series stainless steels, has approximately 16 to 18% chromium, 8 to 10% nickel and up to 3% molybdenum.

When used in seawater, stainless steels resist uniform corrosion but the chloride ions in seawater tend to cause breakdown of the passive film at discrete sites on the metal surface.[3,4] The underlying metal at these sites becomes anodic, while the vast majority of the surface remains passive and becomes cathodic. Once formed, the anode and cathode areas do not shift location, as they do on plain carbon steel, but remain fixed. In addition, the high concentration of metal chlorides that builds up at each anodic site causes the pH of the electrolyte at the anode to become more acidic, and accelerates the rate of attack at these sites.[3,4]

The result is a nigh rate of penetration of the metal at the anodic sites while the rest of the surface remains unattacked. This mode of corrosion, often leading to a series of small holes which perforate the metal, is called "pitting." As a general rule, the fewer pits there are on a given surface, the larger and deeper they will be. As the number of pits increases, the individual pits become smaller and shallower.

Stainless steels are also susceptible to another form of localized attack called crevice corrosion. It takes place within crevices found around threaded fasteners, under washers, gaskets, and O-rings, between the faces of riveted lap joints, and similar places of restricted geometry that are shielded from the water movements that continually

wash the remainder of the surface with fresh, oxygenated seawater. The water inside the crevice becomes stagnant and depleted in oxygen, and the surface in contact with this water becomes the anode, while the remaining surface outside the crevice is the cathode. The mechanism is similar to that of pitting. The pH inside the crevice becomes acidic and the anode reaction becomes self-accelerating. Corrosion starts on the interior surfaces and hollows out the part, as illustrated in Figure 2, until its strength becomes insufficient and it fails.

Factors Affecting Deep Ocean Corrosion Rates

The parameters generally recognized as having an influence on the corrosion rates of steel and stainless steels in seawater are: dissolved oxygen, temperature, salinity, pH, relative velocity of the water, and the presence of fouling organisms.[2,4-7] Figure 3 shows the typical variability of some of these parameters with depth in the Northeastern Pacific Ocean.[6] Let us consider their effects first on plain carbon structural steel and then on stainless steels. For purposes of this discussion, the deep ocean shall be defined as any depth greater than 2000 meters.

On structural steels, the corrosion rate is a direct function of the dissolved oxygen concentration of the seawater.[4-7] This effect is so strong that it tends to overshadow everything else. The corrosion rate of steel is also a direct function of temperature. When oxygen concentration is the rate controlling factor, as it usually is in seawater, the corrosion rate of steel is estimated to be halved by each 30°C decrease in temperature.[4] Nevertheless, the influence of temperature on corrosion rates is weaker than that of dissolved oxygen. An

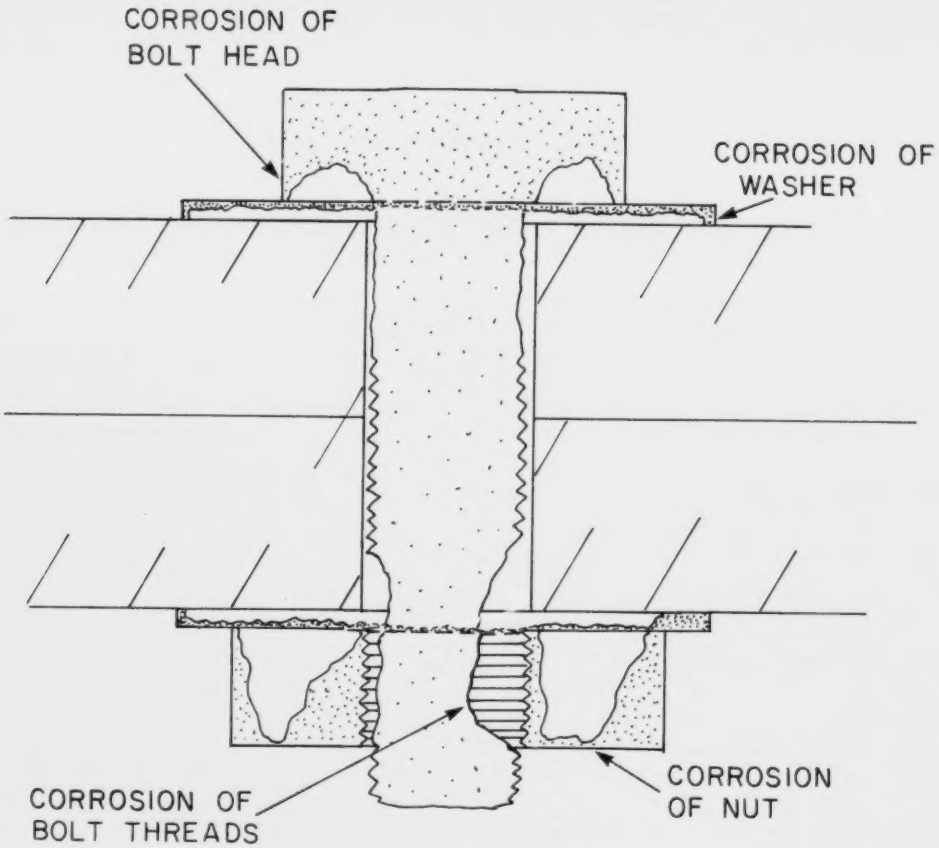

FIGURE 2. Crevice corrosion sites around a mechanical fastener.

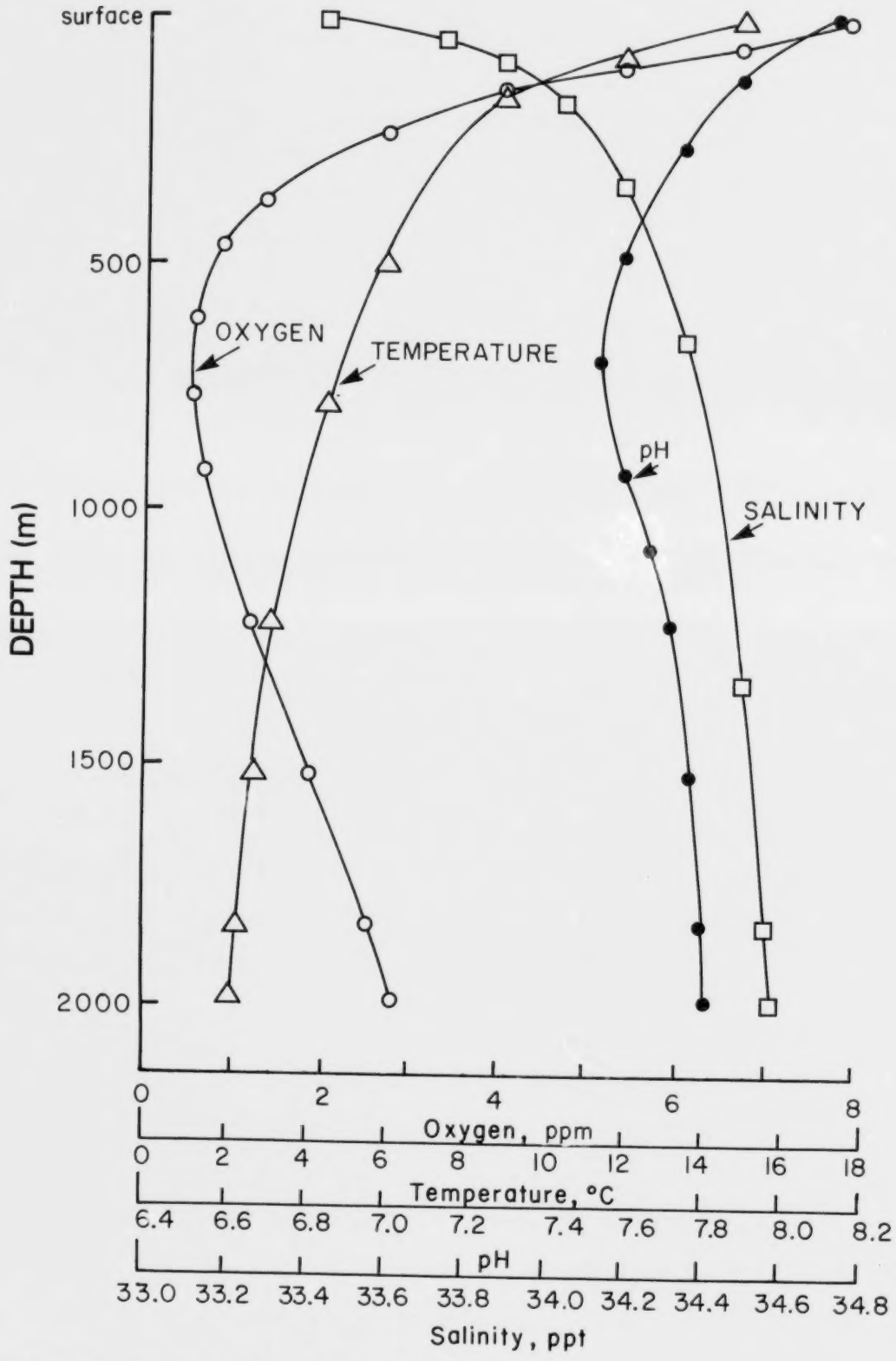

FIGURE 3. Variability of oceanographic parameters in the Pacific Ocean off Port Hueneme California (After Reinhart[6])

example of the overriding effect of dissolved oxygen in the deep ocean is shown in Figure 4, where the corrosion rate, expressed as mils per year (mpy), increases again with increasing dissolved oxygen concentration at greater depths despite a continual decrease in temperature.[6]

The salinity and pH of seawater have only a small effect on the corrosion rate of steel. When considered as a function of salinity, the corrosion rate reaches a maximum at a value of about 35 °/oo (parts per thousand) salt content and decreases gradually at higher and lower values.[4] This maximum is the result of two competing tendencies. First, the conductivity of seawater increases with increasing salinity, resulting in a greater separation between the anode and cathode areas, and consequently a less protective corrosion product (rust) film.[4] This accounts for the initial increase in corrosion rate with increased salinity. Second, the solubility of dissolved oxygen decreases with increasing salinity. This latter effect becomes predominant at about 35 °/oo salinity, thus accounting for the gradual decrease in corrosion rate at higher salinity.[4] Over the normal range of open ocean salinities, however, the changes in corrosion rate with salinity are so small as to be completely overshadowed by the effects of dissolved oxygen.[5-7] Within the normal slightly alkaline (pH 7.4-8.4) range of open ocean pH, the corrosion rate of steel is independent of pH.[7] Below pH 4, the corrosion rate increases rapidly with increasing acidity. Above pH 10 the corrosion rate decreases, and approaches zero at pH values greater than 12.[4]

At water velocities exceeding 3 to 4 meters per second, the corrosion rate of steel rapidly increases.[2] This is especially true in cases where there is appreciable suspended particulate matter in the

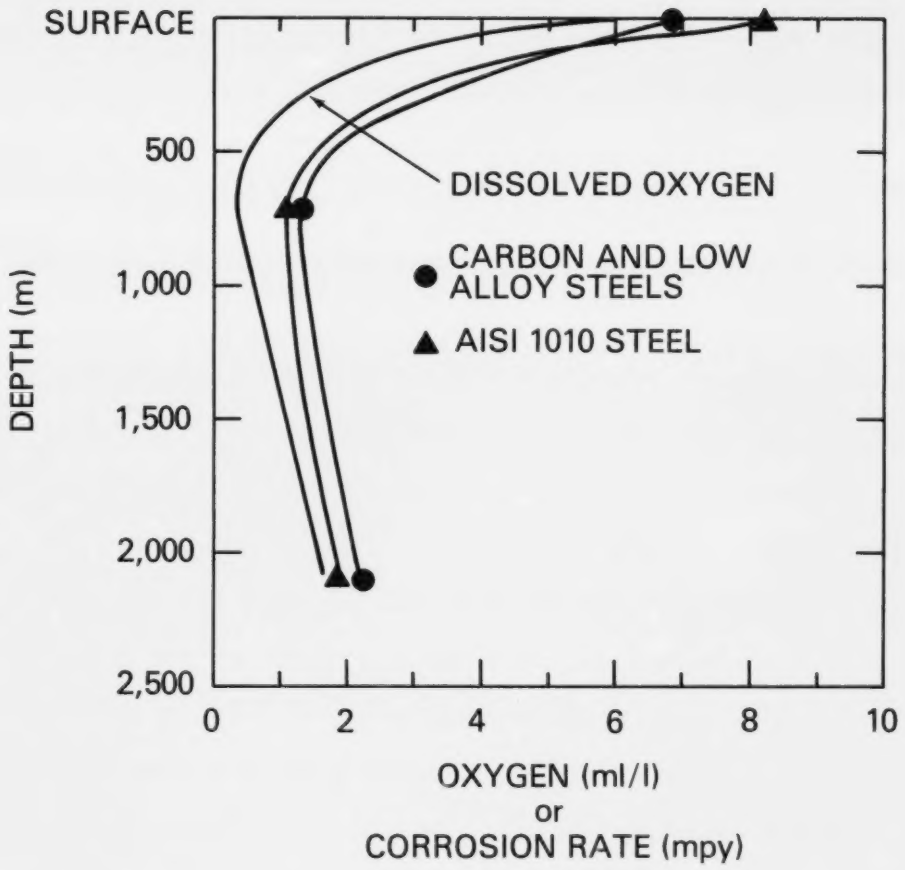

FIGURE 4. Corrosion rate of structural steels as a function of depth and dissolved oxygen. (After Reinhart[6]).

seawater that might lead to abrasion of the surface and the removal of corrosion product films. Deep ocean currents, however, usually have much smaller velocities than this (3 to 30 cm per second is typical[8]) and are not expected to play a substantial role in determining the corrosion rate.

Macroscopic marine fouling organisms do not usually have an adverse effect on the corrosion rate of structural steels. In fact, a complete cover of hard-shelled sedentary (sessile) fouling organisms may decrease the corrosion rate by acting as a barrier through which dissolved oxygen must diffuse to reach the metal surface.[4,6,7] Such a complete layer of organisms is rare in the deep ocean. There are fewer biofouling organisms present at great depths, and those that are present near the bottom tend to attach as opportunistic individuals, causing only a slight perturbation of the corrosion rate in their immediate vicinity.[9,10] Fouling is expected, therefore, to have only a minor effect on the overall corrosion rate of steels in the deep ocean.

Marine microorganisms can influence the corrosion rate of steels only in restricted areas where they can change the chemistry of the surroundings. For instance, the corrosion rate of steel can be appreciable in anaerobic bottom sediments if sulfate-reducing bacteria are present. The mechanism of this type of attack will be considered later in this report.

These same parameters have different effects on the corrosion rate of stainless steels, which corrode by pitting and crevice corrosion rather than by uniform attack.[4-6] The factors that influence these localized forms of attack are primarily those that allow or discourage differences in the environment from place to place on the metal surface.

Dissolved oxygen has a major effect only when differences in it are permitted to develop along the metal surface. This happens most readily in stagnant or zero velocity conditions or when crevices, such as shown in Figure 2, are built into the mechanical design. Seawater velocities of 1.5 to 2 meters per second can suppress the initiation of pitting corrosion altogether by keeping the surface uniformly immersed in oxygenated water.[2] Water velocity has little effect on crevice corrosion, however, because the corroding surface is shielded from the flow of water.

The above effects are in direct contrast to the case for plain carbon steels, where an increase in velocity brings more oxygen to the corroding surface and increases the corrosion rate. Another direct contrast to the case for plain carbon steels is that of fouling organisms. On plain carbon steels these organisms tend to decrease the corrosion rate by acting as a diffusion barrier for dissolved oxygen. On stainless steels, however, unless the fouling layer is complete and uniform, it creates localized oxygen-shielded regions and promotes crevice corrosion beneath the organisms.

Temperature has the same effect on stainless steels that it has on plain carbon steels, and to a first approximation, the salinity and pH of seawater have little effect on the rate of pitting and crevice corrosion of stainless steels.

Historically, when stainless steels have been present in low-level nuclear waste packages from ocean disposal, they have been as part of the waste form itself embedded in the concrete. Thus, the environment to which stainless steels have been subjected is neither open ocean seawater nor bottom sediment, but rather seawater-saturated concrete,

the pH of which is normally 12 to 14. This alone should suppress the initiation of pitting, because hydroxyl (OH^-) ions have been found to be effective inhibitors for pitting in stainless steels.[4] The alkaline pH will also inhibit corrosion if the core is made of structural steel. As long as the dissolved oxygen level is maintained uniformly low and the pH uniformly high over the entire surface of the metal, very little corrosion might be expected whether the metal is made of structural steel or stainless steel.

There are two ways in which this desirable low oxygen, high pH environment may be lost. The first way is if the concrete itself deteriorates according to one of the mechanisms discussed in the next section. If the concrete becomes fractured and allows oxygenated seawater to contact part of the metallic waste form, corrosion will start. For stainless steel, the exposed area will become cathodic and the remaining surface still shielded by the concrete will be susceptible to crevice corrosion. For structural steel, uniform corrosion will start on the surface exposed to ambient seawater and the wedging action of the corrosion products, which are more voluminous than the steel from which they form,[3] will tend to pry the concrete away and progressively expose more steel.

The second way the desirable environment can be lost involves changes in internal chemistry that occur as the concrete absorbs seawater over a period of time. Recent evidence[11] indicates that as the pores (or voids) in the concrete become saturated with seawater, chloride ions from the absorbed seawater break down the protective film on the metal surface and initiate corrosion. As corrosion proceeds, the

metal-chloride corrosion products, which are acidic, both reduce the pH of the pore water, and produce the wedging action mentioned above. Both these effects tend to produce still more corrosion.

2.2 DETERIORATION OF CONCRETE

The primary mechanism of degradation of portland cement type concretes in seawater is sulfate attack.[12] In waters with more than about 2000 ppm sulfate, destructive chemical reactions can take place with the cementing constituents of the concrete.[12,13] Since the average concentration of SO_4^{--} ions in the Atlantic Ocean is 2810 ppm,[7] this type of attack can and does take place.[12]

Destructive attack can follow either or both of the following two modes:[12] (1) cracking due to the formation of a calcium-sulfoaluminate hydrate called ettringite, or (2) surface softening due to the formation of gypsum. The first type of attack can take place in portland cements containing more than 5% of tricalcium aluminate ($3CaO \cdot Al_2O_3$). The sulfates react with hydrated $3CaO \cdot Al_2O_3$ in the presence of calcium hydroxide ($Ca(OH)_2$) to form ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaO \cdot SO_3 \cdot 32H_2O$). Ettringite has a strong tendency to absorb water. This causes it to expand and results in cracking of the concrete. In the second type of attack, acidic sulfates cause the conversion of $Ca(OH)_2$ to gypsum ($CaSO_4 \cdot 2H_2O$) according to the following reaction:

$$Ca(OH)_2 + MgSO_4 \cdot 7H_2O \rightarrow Mg(OH)_2 + CaSO_4 \cdot 2H_2O + 5H_2O$$

This is accompanied by surface softening and spalling of the concrete. The types of attack discussed above are aggravated by high porosity as well as by high $3CaO \cdot Al_2O_3$ and $Ca(OH)_2$ contents in the cement phase.

3.0 ENVIRONMENTAL DATA

3.1 STRUCTURAL STEEL

There is a considerable volume of data on the corrosion of plain carbon structural steel in natural seawater. The bulk of these data are for shallow coastal water exposures. In general, the shallow water data show initial uniform corrosion rates as high as 380 micrometers per year (μm/y), decreasing with time to a constant value of 75 to 125 μm/y after two or three years of exposure.[2,5,14-16] The rate at which the uniform corrosion rate decreases depends upon how quickly the barrier film of corrosion products, carbonaceous deposits, and fouling organisms builds up, and upon how effective this film is in preventing dissolved oxygen from reaching the bare metal surface. Once this film has formed, factors which may cause the corrosion rate to vary outside the 75 to 125 μm/y limits are pollution (especially by sulfides), high water velocities, or variations in water temperature. In addition, very low dissolved oxygen can reduce the rate to less than 75 μm/y.

The corrosion is not always entirely uniform. Localized attack in the form of broad shallow pitting has frequently been reported with penetration rates of up to 10 times the uniform corrosion rate. Occasionally, a very deep pit will be observed. For instance, a pit with a depth of 4 mm was observed on one panel that had been exposed for 16 years in the Pacific Ocean at the Panama Canal Zone.[17] The pitting type of attack tends to be more severe in polluted seawater and on materials from which the mill scale is not cleaned off properly.[4,5]

In the deep ocean, which is the primary focus of this report, the corrosion rates of plain carbon steels tend to be lower than they are in surface waters.[5,15] The rate of attack decreases with time in deep

waters, as it does in shallow water, starting at 50 to 100 μm/y and decreasing to 12 to 50 μm/y.[15] Several factors favor lower corrosion rates in the deep ocean. The most prominent of these is low dissolved oxygen. The decrease in dissolved oxygen with depth is more pronounced in the northeastern Pacific Ocean than it is in the northwestern Atlantic, where the minimum in dissolved oxygen is generally not as low, and where the value at great depths can be as high as, or higher than it is at the surface.[5,18] Table II shows that for plain carbon steel exposed at similar depths in the Atlantic and Pacific Oceans, the corrosion rate is doubled in the Atlantic because of the higher dissolved oxygen. For a given oceanic site, therefore, the concentration of dissolved oxygen must be known before any prediction of the corrosion rate can be made.

Other factors favoring low corrosion rates in the deep ocean are low water velocities and low temperatures. The decrease in corrosion rate with time is usually more gradual in the deep ocean than it is in surface waters because protective surface films form more slowly under deep ocean conditions. The low temperature and more acidic pH retard the rate of deposition of carbonaceous type mineral scales,[5,19] and fouling films form slowly if at all.[9,10]

TABLE II

CORROSION RATE OF STEEL AFTER 3 YEARS EXPOSURE

Location	Depth	Temperature	Dissolved Oxygen	Corrosion Rate	Reference
Pacific Ocean	1675 m	6.65°C	1.5 mℓ/ℓ	25 μm/y	14,15
Atlantic Ocean	1515 m	4.18°C	5.7 mℓ/ℓ	50 μm/y	14

Since the low-level nuclear waste containers that have previously been deposited in the ocean are sitting on the bottom partially embedded in the sediments, corrosion rates in these sediments are an important consideration. Generally, corrosion rates of steel in the sediments will not differ greatly from those in the water immediately above the sediments.[5] However, there are several factors that can cause corrosion rates in the sediments to be different from those in the water. These factors include: (a) a difference in concentration of some chemical species, such as dissolved oxygen, between the sediments and the water, (b) the presence or absence in the sediment of sulfate reducing bacteria under anaerobic (no dissolved oxygen) conditions and, (c) the presence of bottom currents strong enough to keep appreciable particulate matter in suspension. Each of these factors will now be discussed in more detail, first for an unpainted steel cylinder, and then for a painted steel cylinder similar to the radioactive waste containers under consideration.

The dissolved oxygen concentration is often lower in the sediments than in the water. This difference produces what is commonly called an oxygen concentration cell. Whenever such a concentration difference exists, it sets up a potential difference resulting in the area of lower oxygen concentration becoming anodic and the area of higher oxygen concentration becoming cathodic. For an unpainted steel cylinder, the portion of the surface exposed to the lower oxygen concentration (i.e., the portion buried in the sediments) would become anodic and suffer a moderately accelerated rate of attack compared to that portion exposed directly to the water.[4]

If dissolved oxygen is completely absent from the sediments, the corrosion rate of steel in the sediments would normally be negligible[4,20] but may be accelerated in the presence of anaerobic, sulfate-reducing bacteria.[5] Such bacteria are almost universally found in the sediments under shallow natural waters, where the dissolved oxygen is used up by decaying organic matter.[20] In deep sea conditions where the amount of decaying organic matter may be very low, however, the presence of sulfate-reducing bacteria may be more variable. In the presence of these bacteria, corrosion rates of steel can be increased by as much as several orders of magnitude. Under anaerobic conditions, the cathodic reaction shifts from the reduction of oxygen described earlier (Section 2.1) to reduction of hydrogen according to the reaction:

$$H^+ + e^- \rightarrow H^\circ$$

Without sulfate reducing bacteria present, the cathodic surface quickly becomes covered with a monolayer of neutral hydrogen atoms (H°), and corrosion stops. Sulfate reducing bacteria, however, strip off the hydrogen layer, thus allowing corrosion to continue, a process called cathodic depolarization.[21] The bacteria utilize hydrogen in their metabolism to reduce sulfates from decaying organic matter to sulfides. The sulfides, in turn, form an iron-sulfide scale on the steel which is cathodic to a bare steel surface. The sulfide scale thus leads to an additional galvanic corrosion of the bare steel.[20] Sulfate-reducing bacteria are rendered inactive, and their effect on corrosion is stopped, by the presence of even trace amounts of dissolved oxygen. Thus, the mechanism of corrosion described above requires both completely anaerobic conditions and a source of sulfates.

For an unpainted steel cylinder, the differences discussed above between the water and sediments will cause accelerated corrosion of that portion of the steel exposed to the sediments. For a painted steel drum, however, the inverse may be found due to the presence of the paint itself. The paint exposed to the water is in a more dynamic environment and may deteriorate more quickly than that exposed to the sediment, due to surface abrasion and biological fouling. This allows corrosion to begin more quickly on the surfaces of the drum exposed to seawater, while the sub-surface paint coating continues to protect the drum. This appeared to be the case for the container recovered from the northwestern Atlantic Ocean during the 1976 Atlantic dumpsite survey. It suffered very little corrosion on the portion of the cylindrical surface that had been buried in the sediments because the paint coating remained in good condition.[22] Coatings, however, cannot be made perfect enough to provide dependable long-term (greater than about 15 years) protection as will be discussed later in this report.

Higher rates of corrosion can also occur just above the bottom sediments if the seawater currents close to the bottom are sufficiently strong to keep appreciable particulate matter in suspension. In this case, the sediment particles gradually abrade away corrosion product and mineral scale or paint films, thus constantly exposing fresh bare metal. This often happens in shallow coastal waters as a result of tidal current or wave action. It would be unusual to encounter deep ocean currents of sufficient magnitude to cause such abrasive action. However, turbidity currents set up by underwater landslides moving large volumes of sediment at considerable velocity may produce this abrasive action.

In light of the above discussion, the important factors to be considered when evaluating corrosivity to conventional structural steel containers placed in deep sea dumpsites are: the dissolved oxygen concentration in the water and sediments; the presence or absence of sulfates and sulfate-reducing bacteria; and bottom currents or turbidity currents.

3.2 STAINLESS STEELS

Stainless steels are not susceptible to uniform corrosion in seawater. They corrode by localized breakdown of their protective passive film at pits and crevices as discussed in an earlier section of this report. The resulting penetration of the surface is deeper and more rapid than it is on plain carbon steel.

Many types of stainless steel are available today, and a number of these perform well in both the marine atmosphere and in the splash zone above mean high tide level. Nearly all of the conventional alloys, however, perform poorly when fully submerged in quiet seawater for periods exceeding one or two months.[5,23,24] Several recently developed stainless alloys have superior performance when fully submerged in seawater. These alloys will be discussed in a subsequent section.

With one exception, it has not been possible to identify which of the available stainless steel alloys have historically been disposed of as nuclear waste in the ocean. That exception is the pressure vessel of the N/S Seawolf reactor, which was dumped in the Atlantic 2800m nuclear waste dumpsite in 1959, and was constructed of Type 347 stainless steel.[25] For the purposes of this report, therefore, it will be assumed that only the more resistant of the commonly available

grades (300-series stainless steels) were used and our discussion will be limited to stainless steel alloys 302, 303, 304, 316, and 347. The nominal compositon of these alloys is given in Table III.

As explained in an earlier section, the environment surrounding the inner stainless steel waste form is initially seawater-saturated concrete at a pH of 12 to 14 rather than ambient seawater itself. There are no long-term data available for seawater corrosion of stainless steel in concrete, but it is expected that as long as the concrete remains intact and the chloride ion concentration remains low, corrosion rates will be low due to the uniform alkaline environment. If the concrete should spall or crack, however, and expose the stainless steel to ambient seawater, or if chlorides become sufficiently concentrated in the pore water, accelerated attack on the stainless steel may take place.

TABLE III[26]

NOMINAL COMPOSITIONS OF 300-SERIES STAINLESS STEELS

Alloy	% Cr	% Ni	% Fe	% Other Major Alloying Elements	Comments
302	17-19	8-10	Balance	-	
303	17-19	8-10	Balance	0.2 S or Se	Free machining grade, least resistant .
304	18-20	9-12	Balance	-	
316	16-18	10-14	Balance	2 - 3 Mo	Most resistant of group
347	17-19	9-13	Balance	1 - 2 Mn	Weldable grade

All the 300-series stainless steels suffer rapid localized attack by pitting and crevice corrosion in quiescent seawater. Rates of penetration in shallow water as high as 11.5 mm/y by pitting and 1.3 mm/y by crevice corrosion have been reported.[5,27] In the deep ocean, the penetration rates tend to be lower (up to 4 mm/y by pitting and 0.3 to 0.75 mm/y by crevice corrosion) due to the lower dissolved oxygen and temperature.[5,27] The rate of attack can be strongly influenced by seawater velocity. An increase in seawater velocity inhibits pit initiation but accelerates pit growth after the pit has already formed. But a stainless steel form encased in concrete would be shielded from such effects. The rates cited above could be considerably higher if less corrosion resistant grades of stainless steel such as the 400-series were involved.

Crevice corrosion can be avoided by welding parts together rather than using threaded fasteners. Unless the welding is done properly, however, the material can be made sensitive to another type of corrosion called intergranular attack or weld decay.[3] This occurs in the heat-affected zone of the weldment. While the metal is at high temperature during welding, the chromium in the alloy is scavenged out of solid solution by an internal precipitation reaction, leaving a network of chromium-rich particles embedded in an alloy that is no longer stainless (because of the depleted chromium). Corrosion then proceeds rapidly in the depleted regions on either side of the weld, while the remainder of the part remains unaffected.[3] Intergranular attack can be minimized by using specially stabilized grades of stainless steel such as types 304L (low-carbon), 316L, 321 and 347 for any part where welded joints

are anticipated. These stabilized grades have resistances to pitting and crevice corrosion comparable to other type 300-series stainless steels but are more expensive because of the addition of stabilizing elements such as tantalum and columbium (Types 321 and 347), or because of a more complex manufacturing process (Types 304L and 316L). Because of the difficulties discussed above, the conventional 300 series stainless steels are seldom recommended for applications in seawater requiring full immersion for durations exceeding about six months, unless some corrosion protection measures are feasible.

3.3 CONCRETE

The rate of deterioration of concrete in seawater varies with the formulation of the material. Most of the published data on deterioration rates comes from blocks of concrete immersed in Los Angeles Harbor[12] in 1905 and subsequently inspected after 27 and 67 years, and a similar series of tests near Trondheim Harbor, Norway,[28] started in 1936 to 1943. The sulfate type of attack described earlier leading to cracking or surface softening was most severe in tests on high permeability concretes where losses in compressive strength of up to 10% were observed.[12,28] The sulfate type of attack was negligible for high quality formulations using portland pozzolan or portland blast-furnace slag cements of low permeability, low alkalanity and low $3CaO \cdot Al_2O_3$ content. Losses in compressive strength due to sulfate attack and/or water absorption in these high quality concretes rarely exceeded 10% and a strength gain was often reported.[12,28] Damage by rock-boring mollusks was limited to superficial surface scouring if a granite aggregate was used.

The factors of most significance to the problem of nuclear waste containment are water absorption and permeability. Most concretes tested at depth were estimated to absorb a total of 1 to 3 percent by weight of water over an extended period of time (several months or more).[29] Superimposed on this absorption, all concretes were permeable to seawater to some extent. Permeabilities have been calculated from the changes in buoyancy with time for hollow concrete spheres moored at various depths in the ocean.[27,30] This permeability to seawater leaves open the possibility of a hollow concrete container eventually becoming filled with seawater and the subsequent leaching of contaminated water back into the environment. For these reasons, unmodified concrete alone should not be relied upon to isolate even low-level waste for a period as long as 300 years, whether the waste is mixed in with the wet concrete, or placed in a cavity inside a concrete shell.

3.4 EFFECTS OF RADIATION

There are no data in existence on the effects of either high or low-level radiation on corrosion rates in the deep ocean. The data that are available in the open literature are concerned with the effects of radiation on corrosion rates in nuclear reactor environments.[31,32] For stainless steels, these data indicate that radiation generally does not accelerate the corrosion rate.[32] There can even be a slight retardation of the corrosion rate of stainless steels if the radiation intensity is large enough to break down the water surrounding the corroding metal. Breakdown of the water provides more oxygen for repairing the passive film, thus inhibiting corrosion.[32] The opinions relative to the effects of radiation on plain carbon steel are mixed.[32,33] There is some evidence that the corrosion rate is accelerated under high neutron flux,[32]

but this is a much different environment than that to which a low-level radioactive waste container would be exposed in the deep ocean.

It is probably safe to conclude that the radiation intensity produced by low-level waste is unlikely to cause a significant increase in the corrosion rate of either plain carbon or stainless steels in the deep ocean where the temperature remains low and the pressure high. Under deep ocean conditions, it would take a level of radioactivity approaching that found in and immediately around nuclear reactor cores to cause a change in the corrosion rate.

4.0 LIFETIME OF CONVENTIONAL CONTAINERS

Based on the data presented in the previous section, an attempt will now be made to estimate the useful and reliable lifetime over which one can confidently predict that the conventional type of low-level nuclear waste container made from steel, concrete and stainless steel will be able to isolate the waste from man and his food chain in the ocean. For the purposes of this report, the criterion of failure for any given layer of the container will be that it either allows water to contact the next layer in such a way that it will start to deteriorate, or it allows water to contact the waste itself. In order for the environment to be contaminated, water must not only reach the interior of the container but must also find its way back out. The time scale of this process depends upon the failure mode of the container, and can range from a few seconds for a container that fails by implosion to several decades or more for one that fails by seepage (leaking or leaching) through concrete and/or by corrosion of a metallic inner waste form. In the following discussion, the entire container will be considered to have failed as soon as it allows water to contact the waste, and the time for the contaminated water to return to the environment will be neglected.

In some cases, there will be so many unknown factors that it will be impossible to accurately estimate the lifetime. In such instances, the only prudent course of action will be to identify the worst possible combination of conditions and the most rapid deterioration mode, assume that if there are a large number of containers these worst-case conditions will occasionally be met, and base the estimated lifetime on this worst case.

Consider first the outermost mild-steel shell. If we assume a worst-case deep-sea corrosion rate of 100 μm/y for the first year decreasing to a constant 50 μm/y thereafter, a 1.5 mm wall thickness will be entirely consumed in 29 years if the corrosion is uniform. Usually, however, there is some broad shallow pitting in which penetration rates are up to 10 times faster than the uniform corrosion rate. Thus, the wall could be penetrated locally in as little as about three years. In most instances, the steel will last considerably longer than this, as was the case for the containers recovered during the 1976 Atlantic dump site survey.[22] But there is no assurance that this will be the case for all containers.

In actual practice, the steel was not meant to isolate the concrete at all as one end was left open. Even if the end were closed, however, one should not rely on the mild carbon steel to keep seawater from the concrete for more than three years.

Consider next the layer of concrete. It has been estimated that an originally dry, hollow sphere with 15 cm thick walls of high quality concrete would be penetrated by seawater (as evidenced by liquid droplets apppearing on the inside surface) in one to two months under a pressure head corresponding to a depth of 3,660 meters.[34] It has also been estimated that the same concrete wall would be saturated with seawater within six months.[34] By the present definition of failure, therefore, a conventional type container having nonmetallic waste mixed in concrete, and the concrete exposed to seawater on one end would have failed by allowing water from the environment to contact the waste within two to six months after deployment. If the open end of the outer steel container were closed, the time to penetration could be extended

by three years, but this is still short compared to the desired 50- to 300-year isolation period.

For containers with structural steel or stainless steel inner waste forms, the initial saturation of the concrete by seawater would not constitute failure because it would not immediately create a situation in which the structural steel or stainless steel would begin to corrode. Corrosion may start shortly thereafter, however, if chloride ions become sufficiently concentrated in the pore water of the concrete, or if the concrete deteriorates further by cracking, spalling or sulfate attack.

Cracking and/or spalling of the concrete can sometimes take place even before deployment of the container due to shrinkage during curing.[35] This problem can be aggravated by the almost inevitable rough shipboard handling which is well known to all seagoing personnel. The outer steel drum helps to minimize such damage, but even with special handling precautions, one would expect the concrete in a small percentage of conventional type containers to be cracked prior to disposal.

Sulfate attack takes place gradually over a time period of tens of years.[12,13,28] Based on our accumulated experience as outlined in section 2.2, one would not expect a 15 cm wall thickness of high quality concrete, in the absence of chloride ions, to be sufficiently damaged by sulfate attack to allow an underlying steel or stainless steel waste form to corrode for at least 75 years, and perhaps as long as the desired 300 years. The difficulties are that (1) in the configuration of conventional low-level nuclear waste containers, the cracking problem may occasionally render the concrete prematurely useless as a corrosion barrier for any interior metals, and (2) not enough is currently known about the chloride ion problem to allow us to predict how long it will

take to initiate corrosion. Almost certainly, however, the time will be short compared to even the shortest desired containment period (50 years).

Let us now examine what might be done to increase the reliability of these containers in their conventional configuration. The methods available for increasing the lifetime of marine structures fall into four categories. These are: (1) isolation of the structure from the environment by coatings, (2) elimination or control of corrosion by cathodic protection, (3) use of chemical inhibitors (which can be ruled out in the present open ocean situation because of the volume of inhibitor that would be required) and (4) use of materials more resistant to deterioration, which will be taken up in the following section on alternative packaging methods.

Coatings protect against corrosion either by isolating the metal substrate from the environment,[36] or, in the case of metallic coatings, by creating a galvanic corrosion couple where the coating is sacrificial to the substrate.[2-6] Nonmetallic marine coating systems have been improved over the last 10 to 15 years, but none of the currently available systems are capable of protecting the substrate from seawater under fully submerged conditions for more than about 10 years without periodic maintenance.

Sacrificial metallic coatings such as zinc (galvanizing) have been used to protect steel successfully in seawater for short periods of time. As a rough rule of thumb, a zinc coating 0.025 cm thick is sufficient to protect steel from corrosion in seawater for one year. Heavier coatings can extend the protection to two or three years. As was the case with nonmetallic coatings, however, longer-term protection

requires periodic maintenance, and this is not practical for a structure sitting unattended on the seafloor. Thus, coatings are considered capable of extending the lifetime of the present type of low-level waste container for only about 10 to 15 years.

Cathodic protection is the most effective means available for controlling metallic corrosion. It is the only way to reduce the corrosion rate to zero and maintain it that way over an extended period of time.[4] Cathodic protection is achieved by applying an external electrochemical current to the corroding system. The polarity of the external current is opposite to that of the natural corrosion current. The applied current opposes the tendency for metallic ions to enter the seawater, and if made strong enough, will stop corrosion altogether.[4] The applied current must be supplied by either an external electronic power supply or by a sacrificial anode such as aluminum, zinc or magnesium. Unfortunately, either type of system requires that the structure be accessible for periodic maintenance. External power supplies need a source of current and must be monitored periodically to make sure that the proper amount of current is being supplied. Too little current allows some corrosion to take place, while too much current can damage the structure being protected. Galvanic anodes become exhausted and must be replaced every one to three years. For these reasons, cathodic protection is not a practical way of controlling corrosion on structures which must be able to survive for more than a few years unattended in the deep ocean. Thus, it is not expected that cathodic protection will contribute significantly to extending either the average lifetime or the reliability of conventional low-level nuclear waste containers in the ocean.

Based on the discussions above, the performance of an average low-level nuclear waste container as previously configured for ocean dumping is expected to be as follows. Starting from the open end of the container, the concrete should become saturated with seawater within about six months. The condition of the concrete then becomes critical. For most of the containers in which the concrete is not cracked or otherwise damaged, the inner waste form, be it structural steel or stainless steel. should not start to seriously degrade for 75 years or longer. The careful application of marine coatings might extend this time by about 15 years. It is even conceivable that a substantial portion of the containers might succeed in isolating tneir waste from the environment for the desired 300-year period. It is probable, however, that the concrete in a small percentage of containers will become cracked before disposal in the ocean due to shrinkage upon curing, or rough handling or both. In this case, the inner waste form should not be relied upon to resist corroding for more than a few days if made of structural steel, or a few months if made of stainless steel. These times are short compared to even a 50-year containment period.

While marine coatings are capable of adding to the lifetime of the average container whose concrete does not crack, coatings can do nothing about the cracking problem itself. Coatings are thus incapable of improving the reliability of the present containers. The containers are likely to have the same rate of early failures with or without coatings.

In order to significantly increase both the reliability of the containers and the public's confidence in the waste disposal system, it will be necessary to change either the materials of construction or the configuration of the container or both.

5.0 ALTERNATIVES TO PRESENT MATERIALS OF CONTAINMENT

Before any scheme for nuclear waste disposal can be considered to be a viable alternative, it must be capable of winning public confidence. In the case of low-level waste disposal on the deep-sea floor, that confidence must be based upon the public's perceived reliability as well as the actual reliability of the waste package. The problem of nuclear waste is such an emotional issue that the public's confidence, based upon the perceived reliability, is likely to be low unless the actual reliability is very nearly 100%. If ocean disposal of low-level waste is to be resumed, convincing evidence must be presented to show that the probability of a total package failure, allowing the seepage of contaminated water into the environment, is negligible over the necessary containment period, even for a large number of packages.

In order to achieve such confidence, a multi-layered package having the following characteristics is recommended: (1) the waste should be encapsulated in an inner core made of an impervious material that will resist corrosion for the duration of the required containment period even if inadvertently exposed to seawater during or shortly after disposal. (2) The inner core should be surrounded with at least 15 cm of an incompressible nonmetallic material that will neither crack nor absorb seawater but that will provide a uniform environment for the core if seawater does get in. (3) The package should be one solid incompressible mass to eliminate the possibility of implosion under pressure. (4) The outer shell should be of a noncorroding material capable of withstanding shock loading and rough treatment at sea.

For the 50-year containment period, it should be possible to build such a waste package. It is not the purpose of this paper to present a detailed design, but some recommendations based upon the characteristics outlined above can be made. A schematic cross section of a conceptual package design is shown in Figure 5.

5.1 INNER CORE

Consider first what would happen if the inner core were made of plain carbon steel or one of the 300 series stainless steels. In either case, corrosion could begin as soon as chloride ions from the seawater caused the pH of the pore water in the concrete to fall below about 4. For structural steel, this will be uniform corrosion. Such a core might last a relatively long time compared to stainless steels. For example, if a wall thickness of 6.5 mm of a particular structural steel is needed to resist deep ocean pressures, then at normal deep ocean corrosion rates, a total wall thickness of 13 mm should last about 125 years before the inner core implodes or begins to leak. A total wall thickness of 2.5 cm might be expected to last the desired 300 years if the corrosion remained uniform. If there were any non-uniformities to the distribution of the corrosion over the surface however, the penetration rate would be faster than that for uniform corrosion. The increase in the penetration rate would be proportional to the degree of non-uniformity and could vary from 1.5 to 100 times the uniform corrosion penetration rate.

If the core material were a 300 series stainless steel, either pitting or crevice corrosion or both could take place, although crevice corrosion is more likely to be the dominant mode in this case because

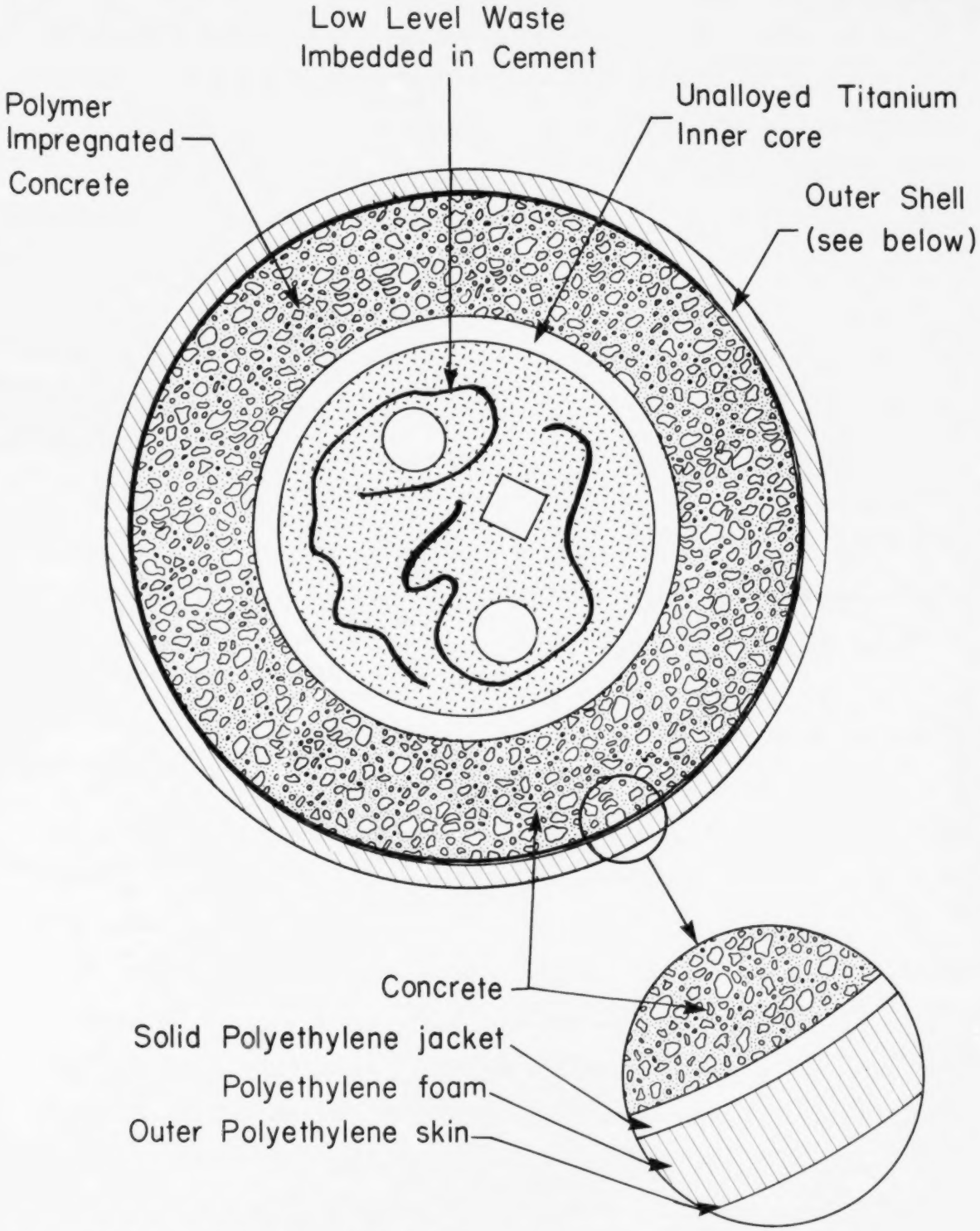

Figure 5. Schematic cross section of proposed low-level waste package.

of the restricted geometry. For either the crevice corrosion or pitting modes, it is difficult to predict how fast the stainless steel core would be penetrated, as the corrosion rate depends on a number of unknown factors. One of the more important of these is the amount of stainless steel surface area that is exposed to ambient seawater. This area will become the cathode, and the larger it is, the more rapidly will the rate-controlling oxygen-reduction reaction be able to proceed. The exposed area could range from less than 1 square millimeter in the case of a small crack up to several square centimeters if a large chunk of concrete spalls off. Assuming the worst case conditions, where a substantial area of 0.5 cm thick stainless steel is exposed, the data presented earlier in this report suggest that penetration of the container could take place in as little as 5 years by a pit on the cylindrical surface or 35 years by crevice corrosion. These numbers could be adjusted up or down for different wall thicknesses, but again, they are shorter than the desired lifetime of 50 to 300 years.

In addition, there is another mode of attack which could be even more rapid. This would involve corrosion at the point where a stainless steel core was sealed after emplacement of the waste. If sealing were accomplished by bolting the end cap to a flange containing a rubber O-ring or a gasket, then crevice corrosion may take place preferentially in the groove holding the O-ring or gasket in place as has often been the case with pressure casings for oceanographic instrumentation. Once corrosion has tunneled under the O-ring, the container will leak, resulting in failure by the present definition. Such failure in stainless steel instrument casings similar in size to a hypothetical waste container core have sometimes occurred within 6 to 18 months of seawater

service. In oceanography, these casings are used only for relatively short-term immersions (1 hour to 1 month) and are given periodic preventive maintenance. Such maintenance is not presently available for a low-level waste container once it has been placed on the sea floor. One can conclude then that plain carbon structural steel and the conventional 300 series stainless steels are not suitable for use as inner core materials. There are, however, other metals with increased corrosion resistance.

The metals and alloys most resistant to both uniform and localized corrosion in seawater include gold, platinum, tantalum, unalloyed titanium and some higher strength titanium alloys, Hastelloy C-276, Inconel 625, and several recently developed stainless steels. The corrosion behavior of all of these has been studied extensively in seawater.[2,4-6,37-39] Gold and platinum can be eliminated because of their low strength and prohibitively high cost. Tantalum, while offering excellent corrosion resistance, is also ill-suited for use as a structural material due to its high cost, low availability and low strength. It is used mostly as a liner in containers for severely corrosive chemicals. The titanium alloys, Hastelloy C-276, Inconel 625 and the new stainless steels, however, are all possible candidates for use as inner core materials.

Unalloyed titanium and two high strength titanium alloys are commonly used in marine environments. The two alloys are Titanium 6 Al, 4V (6-4) and Titanium 6 Al, 2 Cb, 1 Ta, 0.8 Mo (6-2-1). The 6-4 alloy has an excellent strength-to-weight ratio but would have to be downgraded for nuclear waste applications because of a slight possibility of stress corrosion cracking in seawater environments.[5] The 6-2-1 alloy

has good strength and was formulated as a replacement for alloy 6-4 to avoid the cracking problem. It is a much newer alloy, however, and there is less long-term seawater experience with it. For these reasons, unalloyed titanium is probably the preferred choice from the titanium alloys group. Its moderate strength of 50,000 to 90,000 psi should be adequate for the present application, and it has withstood more than 30 years of service in seawater environments at 0°C to 30°C without any reported instances of corrosion of any type. The major disadvantage of all the titanium alloys is their relatively high cost as compared to structural steel.

Hastelloy C-276 and Inconel 625 are both nickel-based chromium-molybdenum alloys, which have long-term seawater corrosion resistances and costs roughly comparable to those of the titanium alloys.[2,37,39] Use of these materials, or one of the titanium alloys, would maximize our confidence in the long-term integrity of the inner core. The titanium alloys have the added advantage of being the lowest in density of any of the candidate inner core materials. Their low density would help to minimize the overall package weight, a matter of considerable importance in shipboard handling.

A series of stainless alloys has recently been developed having greatly improved resistance to crevice corrosion and pitting in seawater[38] as compared to that of the conventional 300 series stainless steels. These are the ferritic and duplex (part ferritic and part austenitic) stainless steels. The most resistant of these are the ferritic stainless steels with 27 to 30% Chromium, 3 to 4% Molybdenum and less than 1% Nickel. These alloys have crevice corrosion resistances under laboratory conditions comparable to that of Hastelloy C-276, although there is

far less service experience with the newer alloys.[38] Other ferritic alloys with 25 to 28% Chromium, 2 to 4% Molybdenum and up to 4% Nickel; plus some of the duplex alloys with 20 to 26% Cr, 5 to 25% Ni and 3 to 7% Mo may also prove to have adequate crevice corrosion resistance. These newer ferritic and duplex alloys have the advantage of being less costly than Hastelloy C-276, Inconel 625 and the titaniums. Their disadvantages are that there is yet far less service experience with them and they are not yet as widely available as the more established alloys. Both these latter two factors are expected to change dramatically, however, within the next 5 years.

There are, thus, a number of alloys now available with greatly improved corrosion resistance compared to the conventional 300 series stainless steels. Any one of the alloys discussed above could probably be used successfully as an inner core material. The final choice of the best alloy will depend on many factors outside the scope of this report, and must await a more detailed package design.

In order to eliminate the possibility of implosion of the inner core under pressure, no matter what its material of construction, it is recommended that once the waste has been placed in the core, cement be injected under pressure to fill any voids and create a solid mass. If the waste were liquid, it could perhaps be mixed with cement, injected into the core and then allowed to set.

5.2 CONCRETE LAYER

The concrete used outside the core should be of high quality, with a low permeability and a granite aggregate as described previously. Water absorption of the concrete can probably be eliminated by using one of the polymer-impregnated concretes that are under development at the

U.S. Naval Civil Engineering Laboratory, Port Hueneme, California,[40] and the Brookhaven National Laboratory, Upton, New York.[41]

5.3 OUTER SHELL

The outer shell should serve two basic functions and perhaps a third. It should serve first as a mold for the concrete, and second as a shock absorber to shield the concrete from the effects of rough handling. It is recommended that the shell be constructed of a rigid polyethylene foam sandwich material as shown by the inset in Figure 5. The outer skin and foam layers will provide shock resistance. These layers will be collapsed onto the inner solid polyethylene jacket by the great hydrostatic pressure of the deep ocean, but this will be of no consequence as they will already have served their function. The polyethylene should be stabilized against ultraviolet radiation using carbon black to prevent deterioration by sunlight between the time of manufacture and of emplacement. Marine exposures of polyethylene for up to seven years usually have resulted in no detectable degradation,[10] and polyethylene has one of the lowest rates of water absorption of all the polymers that have been tested. In addition, polyethylene is relatively immune to marine borer attack when not immediately adjacent to a piece of wood.[10] This material is far less likely to degrade over a 50-year period than is a conventional structural steel shell. A third possible function would be for the inner polyethylene jacket to serve as an additional moisture barrier if some way could be found to seal the outer shell after insertion of the core and concrete.

Such a container could be either cylindrical or spherical in shape. A sphere would be preferable because, under hydrostatic compression, tensile and shear stresses would be minimized. The cylinder, however,

might be more economical and convenient, since tubular mill forms of most materials are readily available. In addition, the cylindrical shape would be easier to handle at sea. There could be a high degree of confidence in such a container of either shape for 50 to 75 years because there is experience with: (1) concrete in seawater for that length of time; (2) titanium, Hastelloy C-276 and Inconel 625 in seawater for about half that time; and (3) the newer candidate materials for at least a few years. It is not possible, however, given our present knowledge of the mechanisms and rates of deterioration of structural materials in the deep ocean, to guarantee the integrity of even this improved container for 300 years. Selected individual containers might well last that long or longer, but there will be uncertainty involved. Therefore, when the desired period of isolation of even low-level nuclear waste in the ocean exceeds the 50- to 75-year period over which actual material exposure tests exist, it is recommended that the waste be disposed of in such a manner that the disposal environment itself provides another barrier to migration of the waste, rather than relying strictly on the packaging materials themselves to do that job.

While a full discussion of additional options to the present methods of nuclear waste disposal is beyond the scope of this report, one would be remiss in making this recommendation without indicating briefly that there is at least one possible additional method already under consideration. Disposal of low-level radioactive waste in stable geologic formations of the deep seabed[42] would seem to be an option compatible with the concept of not requiring or expecting the physical container to permanently isolate the waste. Such depositories are being

discussed and evaluated mainly for high-level waste disposal. However, their most attractive feature -- the potential of being able to chemically bind the waste and thus to isolate it from man and his marine food chains for long periods of time after the deterioration of the original container -- should apply to low- as well as to high-level waste.

At the present time then, the most logical course of action might be to: (1) attempt to develop cost-efficient nuclear waste packaging systems which could demonstrably isolate and contain the wastes for specified periods of time, preferably fifty to three hundred or more years; and (2) couple this packaging system to a carefully selected environmental isolation system (deep-se disposal site) to provide for an additional measure of isolation and containment of the waste after the man-made packaging system has begun to release its contents.

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